United States Patent

Willems et al.

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[54] STABILIZING SILVER IMAGE IN PRESENCE OF HETEROCYCLIC THIOXO COMPOUND CONTAINING SULPHOGROUP

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[30] **Foreign Application Priority Data**

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[52] **U.S. Cl.** **96/61**

[51] **Int. Cl.** **G03c 5/38**

[58] **Field of Search** 96/61, 109, 95

[56] **References Cited**

UNITED STATES PATENTS

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Assistant Examiner—Won H. Louie, Jr.
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[57] **ABSTRACT**

A rapid process for producing a stable photographic image is disclosed which comprises developing an exposed silver halide emulsion layer of a photographic material and treating the developed emulsion layer with a stabilizing solution containing a stabilizing agent such as ammonium thiocyanate and a heterocyclic thioxo compound showing thioxo-thiol tautomerism and corresponding to the formula

wherein Z represents the atoms necessary to close a five or six member heterocyclic nucleus containing at least one sulfo group in acid or salt form. The residual unexposed and undeveloped silver halide which is left in the emulsion layer forms a light inert complex. The thioxo-thiol compound improves the stability of the produced image to light, heat, and humidity.

10 Claims, No Drawings

STABILIZING SILVER IMAGE IN PRESENCE OF HETEROCYCLIC THIOXO COMPOUND CONTAINING SULPHOGROUP

The present invention relates to a process for stabilizing developed photographic images according to which the silver halides remaining after development in the unexposed areas are converted into compounds that are inert to heat, light and humidity, thereby eliminating normal processing operations of fixing and washing.

The normal processing of photographic materials involves the development of the exposed silver halide to a silver image, conversion of the unexposed silver halide to a soluble salt by fixation and removal of the soluble silver salt formed as well as of the fixing solution employed by washing with water.

In many cases it is desirable to produce the photographic record in the least possible time and with a minimum of effort and equipment. Therefore, it has been proposed to eliminate the time-consuming fixing and washing operations by converting, with the aid of stabilizing agents, the unexposed and undeveloped silver halide of the photographic emulsion into colourless light-insensitive compounds, which need not be removed by washing.

The fundamental difference between conventional and stabilization processing is, therefore, that whereas in the former the usual argento-thiosulphate complexes formed during fixing have to be washed out, in the latter the silver complexes are left in the emulsion.

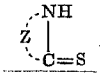
In practice ammonium thiocyanate is widely used as stabilizing agent although it has some disadvantages. Indeed, ammonium thiocyanate produces a high rate of stabilization but the silver image has a great tendency to bleach out or fade upon storage, particularly at high humidity.

In order to prevent fading of the silver image upon prolonged storage, it has been proposed to add heterocyclic thioxo compounds such as 1-phenyl-2-tetrazoline-5-thione as additive to the stabilizing solution. However, these compounds are generally little soluble in acid stabilizing baths so that it is difficult to incorporate them therein in the appropriate concentration. Moreover, said compounds cannot be incorporated into the material itself in the required concentration because they inhibit development.

It has now been found that the stabilizing effect of the stabilizer can be improved i.e., that the loss of image density on storage of the stabilized image can be reduced or eliminated by carrying out the stabilizing treatment in the presence of at least one heterocyclic thioxo compound showing thioxo-thiol tautomerism and comprising in its molecule at least one sulpho group in acid or salt form.

Thus, in accordance with the present invention a method is provided for producing images that are stable to light, heat and humidity, and have much less propensity to fade or become stained on prolonged storage, which method comprises exposing a photographic material comprising at least one light-sensitive silver halide emulsion layer, developing the exposed material and treating the material with a stabilizing composition, by which the residual unexposed silver halide is converted into a light-insensitive compound, wherein said treatment occurs in the presence of at least one heterocyclic thioxo compound showing thioxo-thiol tautomerism and comprising in its molecule at least one sulpho group in acid or salt form.

The heterocyclic thioxo compounds of use according to the present invention can be represented by the following general formule:



wherein Z represents the atoms necessary to close a 5- or 6-membered heterocyclic nucleus including a heterocyclic nucleus comprising a fused aromatic ring system for instance a fused benzene or naphthalene ring, preferably a benzo- or

naphtho-imidazoline, -oxazoline or -thiazoline nucleus, a diazoline nucleus, a triazoline nucleus, a thiadiazoline nucleus, an oxadiazoline nucleus, a tetrazoline nucleus, a thiadiazine nucleus, a benzthrazolotriazine nucleus, a pyridine nucleus, a pyrimidine nucleus, a pyridazine nucleus or a triazine nucleus, the molecule containing at least one sulpho group in acid or salt form e.g., a salt of an alkali metal or alkaline earth metal, such as sodium, potassium and barium, ammonium, an organic base such as an amine, a soluble zinc salt, etc.

Of course, the heterocyclic thioxo compounds of use according to the present invention may be substituted in the aromatic or heterocyclic ring(s) in so far as these substituents do not adversely affect the image quality and the physical properties of the compounds. Examples of suitable substituents are: alkyl of at most five carbon atoms including substituted alkyl e.g., hydroxyalkyl, aralkyl including substituted aralkyl, aryl including substituted aryl, alkoxy of at most five carbon atoms, halogen e.g., chlorine, alkoxy-carbonyl, nitro, amino including substituted amino e.g., acylamino, carboxyl, etc.

The invention is of particular value in the processing where (a) photographic developing agent(s) is (are) contained in the photographic material, the development is activated by means of an alkaline activator bath and the stabilizer is a solution containing known stabilizers; these known stabilizers or silver-complexing agents include thiosulphates, thiocyanates, thioureas, thioglycollic acid, thiosalicylic acid, thiopyrimidines, etc.—ammonium, potassium and sodium thiocyanate are preferably employed.

Examples of compounds corresponding to the above general formula and suitable for use according to the present invention are:

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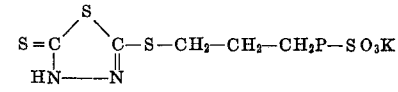

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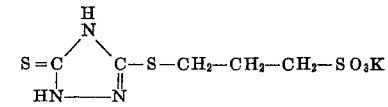

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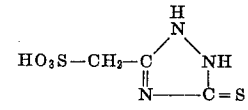

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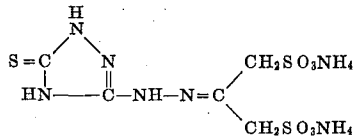

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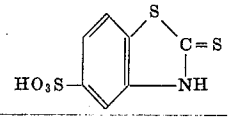

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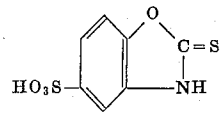

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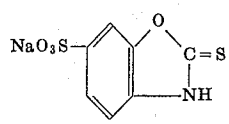

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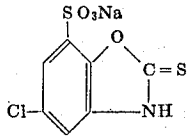

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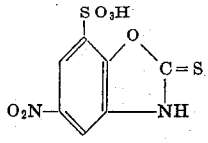

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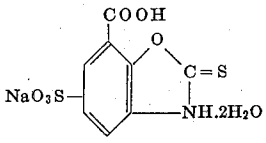

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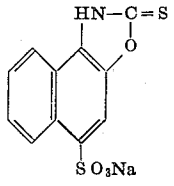

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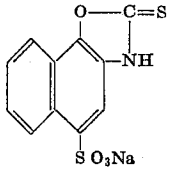

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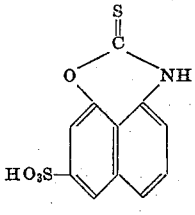

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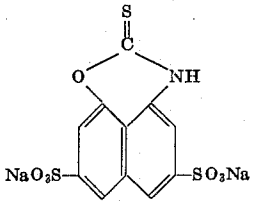

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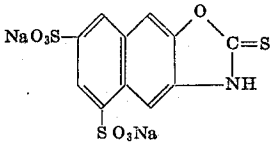

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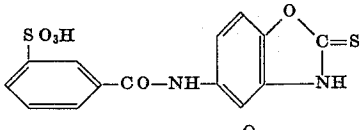

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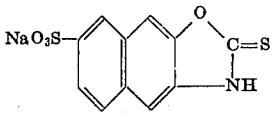

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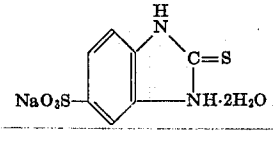

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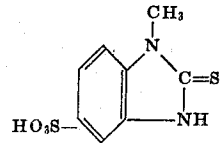

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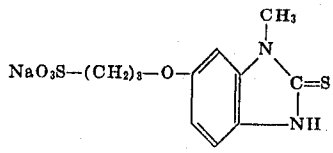

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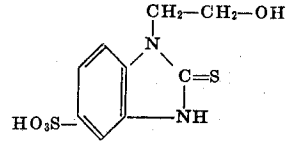

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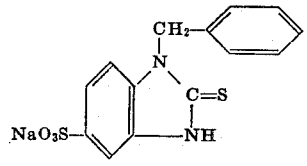

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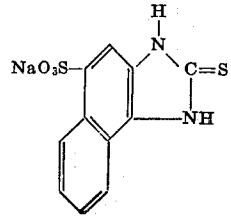

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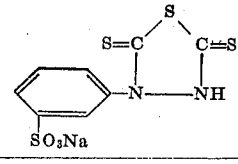

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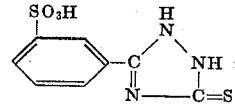

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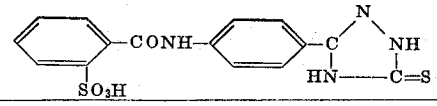

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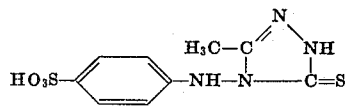

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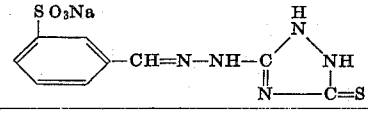

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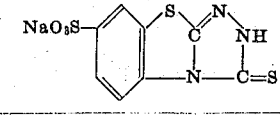

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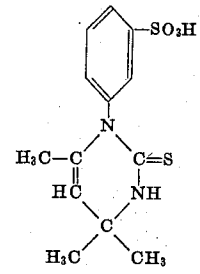

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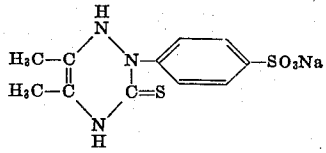

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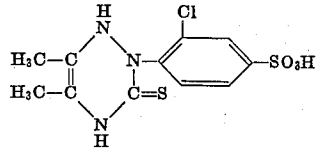

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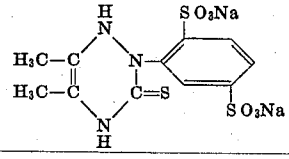


The compounds of use according to the present invention are not only suitable for being incorporated into the stabilizing solution in which they dissolve readily but they are also particularly suitable for being incorporated into at least one of the colloid layers of the photographic material, preferably into the silver halide emulsion layer, since they can be incorporated therein the required concentration without giving rise to a marked desensitization of the photographic material, which is the case, as already said above, with most known heterocyclic mercapto compounds comprising no solubilizing sulpho group. In addition thereto the high water-solubility guarantees a homogeneous distribution of the compounds according to the invention in the coating composition of the layer into which they are intended to be incorporated. Since the compounds of the invention form soluble silver complexes with the residual silver halide, less stain is produced in the highlight areas of the image on ageing because some of the silver complex diffuses from the material into the stabilizing solution. Moreover, in cases where a very high degree of stabilization is required the concentration of the soluble silver complexes formed in the material with the compounds of use according to the invention can be reduced by a post-stabilization treatment consisting of a short rinsing with water.

The amount of compound according to the above general formula to be used can vary within very wide limits and depends on the nature of the particular compound and on the photographic material for which it is used. The optimum amount can be readily determined for each particular material by simple tests. Generally said compounds are employed in the stabilizing bath in amounts from about 0.1 g. to about 10 g., preferably from about 0.5 to 5 g., per litre of composition, and in the photographic material in amounts from about 10 mg. to about 2 g. preferably from about 50 mg. to about 0.5 g. per mole of silver halide.

The photographic emulsions may be of any type, e.g., they may be spectrally sensitized or nonsensitized emulsions and various silver salts may be used as light-sensitive salt e.g., silver bromide, silver iodide, silver chloride or mixed silver halides e.g., silver chloro-bromide, silver bromo-iodide and silver chlorobromo-iodide.

The silver halides are dispersed in the common hydrophilic colloids e.g., gelatin, casein, polyvinyl alcohol, carboxymethyl cellulose, alginic acid etc., gelatin being however favoured.

The light-sensitive emulsions may be chemically as well as optically sensitized. They may be chemically sensitized by effecting the ripening in the presence of small amounts of sulphur containing compounds such as allyl thiocyanate, allyl thiourea, sodium thiosulphate, etc. The emulsions may also be sensitized by means of reductors for instance tin compounds as described in French Patent Specification 1,146,955 and in Belgian Patent Specification 568,687, imino-amino methane sulphinic acid compounds as described in British Patent Specification 789,823 and small amounts of noble metal compounds such as of gold, platinum, palladium, iridium, ruthenium and rhodium. Further the light-sensitive emulsions may be sensitized by addition of development accelerators as for example compounds of the polyoxyalkylene type such as alkylene oxide condensation products as described among others in U.S. Pat. Nos. 2,531,832 and 2,533,990, in United Kingdom Pat. Nos. 920,637, 940,051, 945,340 and 991,608 and in Belgian Pat. No. 648,710 and onium derivatives of amino-N-oxides as described in published Dutch Patent Application 6612269.

The light-sensitive emulsions may also comprise one or more developing agents such as hydroquinone, 1-phenyl-3-pyrazolidinone, *p*-aminophenol and *p*-phenylene diamine derivatives etc., antioxidantia for said developing agents such as potassium metabisulphite, matting agents, etc.

As already indicated above it is preferred to incorporate at least part and preferably even the total amount of developing substance(s) into the light-sensitive material. In this way the developer can be reduced to a mere aqueous alkaline activator bath, which by the absence of developing agent(s) is better keepable.

The following examples illustrate the use of the compounds according to the invention.

EXAMPLE 1

A gelatino silver chlorobromide emulsion (60 mole percent AgBr and 40 mole percent AgCl) containing hydroquinone and potassium metabisulphite as well as other common emulsion ingredients such as sensitizing agents, hardening agents and coating aids, is coated on a conventional film support and dried.

The photographic material obtained is exposed and developed e.g., in a developing bath comprising per litre 60 g. of sodium hydroxide, 40 g. of anhydrous sulphite, 2 g. of potassium bromide and 1 g. of 1-phenyl-3-pyrazolidinone.

Then the exposed and developed material is treated in a stabilizing bath having the following composition:

ammonium thiocyanate	250 g.
potassium metabisulphite	145 g.
30 % formaldehyde	120 ml.
60 % acetic acid	25 ml.
compound 22	1 g.
water to make	1 liter.

After having been dried the image treated with the above composition shows good stability against fading of the image silver and staining of the highlight areas. Indeed, even when having been kept for 18 days in an atmosphere of 20°C. and 60 percent of relative humidity or exposed for 1 month to direct daylight the density of the image has faded less than that of an image treated with an analogous composition but without the compound according to the invention and the highlight areas are less stained.

The same favorable results are obtained when replacing compound 22 by a same amount of one of the compounds 2, 5, 7, 16, 26 of the above list of compounds.

EXAMPLE 2

To a gelatino silver chlorobromide emulsion (60 mole percent of AgBr and 40 mole percent of AgCl) containing hydroquinone and potassium metabisulphite as well as other common emulsion ingredients such as sensitizing agents, hardening agents and coatings aids 0.1 g. of compound 15 is

added per mole of silver halide. This emulsion is then coated in the conventional manner on a baryta coated paper support and dried.

The material obtained is exposed and developed e.g., in a developing bath comprising per litre 40 g. of sodium hydroxide, 40 g. of anhydrous sodium sulphite, 2 g. of potassium bromide and 1 g. of 1-phenyl-3-pyrazolidinone.

Then the exposed and developed material is treated in a stabilizing bath as described in example 1 comprising however no compound 22.

After having been dried the image obtained shows as compared with a material comprising no compound according to the invention, good stability against fading of the image silver and staining of the highlight areas on storage.

We claim:

1. In a rapid process for producing a stable photographic image which comprises developing an exposed silver halide emulsion layer of a photographic material and treating the developed emulsion layer with a stabilizing solution containing at least one stabilizing compound selected from the group consisting of alkali metal and ammonium thiocyanates and thiosulphates, thioureas, thioglycollic acid, thiosalicylic and thiopyrimidines as stabilizing agent to form with residual unexposed and undeveloped silver halide a light-inert complex which is left in the emulsion layer, the improvement which comprises treating the developed emulsion layer with the said stabilizing solution in the presence of at least one heterocyclic thioxo compound showing thioxo-thiol tautomerism and corresponding to the formula:

wherein Z represents the atoms necessary to close a 5- or 6-membered heterocyclic nucleus selected from the group consisting of imidazoline, oxazoline, thiazoline, diazoline, triazoline, thiadiazoline, oxadiazoline, tetrazoline, thiadiazine, benzthiazolotriazine, pyridine, pyrimidine, pyridazine, and triazine; and said heterocyclic nuclei comprising a fused aromatic ring and on the molecule at least one sulpho group in acid or salt form.

2. Method according to claim 9, wherein Z represents the atoms necessary to close a benzoxazo line nucleus, a benzothiazoline nucleus, a benzoimidazoline nucleus, a naphtho-imidazoline nucleus, a naphthoxazoline nucleus, a naphtho-thiazoline nucleus, a diazoline nucleus, a triazoline nucleus, a thiadiazine nucleus, a benzthiazolotriazine nucleus, a pyridine nucleus, a pyrimidine nucleus, a pyridazine nucleus, or a triazine nucleus.

3. Method according to claim 1, wherein said heterocyclic compound is present in the said stabilizing solution.

4. Method according to claim 1, wherein said heterocyclic compound is present in the said stabilizing solution in an amount of about 0.1 g. to about 10 g. per litre.

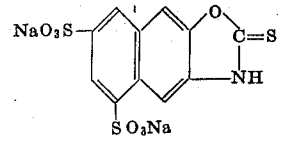
5. Method according to claim 1, wherein said photographic material includes a colloid layer and said heterocyclic compound is present in said colloid layer of the photographic material.

6. Method according to claim 1, wherein said heterocyclic compound is present in said light-sensitive silver halide emulsion layer of the photographic material.

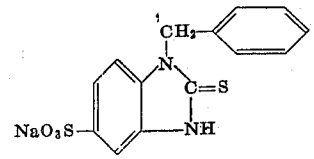
7. Method according to claim 1, wherein said heterocyclic compound is present in said light-sensitive silver halide emulsion layer of the photographic material in an amount of about 10 mg. to about 2 g. per mole of silver halide.

8. The process of claim 1 wherein the stabilizing compound is an alkali metal or ammonium thiocyanate.

9. The process of claim 8 wherein the thioxo compound has the formula



10. The process of claim 8 wherein the thioxo compound has the formula



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